RESEARCHERID
THOMSON REUTERS

[Mondal*, 7(3): March, 2018]
IC™ Value: 3.00

ISSN: 2277-9655
Impact Factor: 5.164
CODEN: IJESS7

IJESRT

INTERNATIONAL JOURNAL OF ENGINEERING SCIENCES & RESEARCH TECHNOLOGY

# SURFACE MORPHOLOGICAL, STRUCTURAL AND HYDROGEN SENSING CHARACTERIZATION OF PD DOPED ZnO THIN FILMS DEPOSITED BY SILAR

**Shampa Mondal***
Assistant Professor, Dept. of Physics
AKPC Mahavidyalaya, Bengai, Hooghly Pin-712611,India

**DOI**: 10.5281/zenodo.1199360

## ABSTRACT

Both Zinc Oxide(ZnO) and Palladium (Pd) doped ZnO thin films prepared by Successive Ionic Layer Adsorption and Reaction technique called SILAR from Sodium Zincate complex. For the structural and morphological studies of the thin films X-ray diffraction(XRD) and Scanning Electron Microscopy (SEM) has done . Strong preferred c-axis orientation happen in both the undoped and Pd-doped ZnO thin films. SEM micrograph reveals that ZnO possess round shaped particles whereas Pd-doped ZnO shows off-sherical particles and compact grains. EDX done for investigating Pd incorporation in the film. Hydrogen ($H_2$) sensing properties of Palladium(Pd) doped ZnO thin films has been studied. behaviors of the ZnO – based gas sensor For 10% Pd doped ZnO, the sensitivity and response time behaviors to hydrogen gas were investigated . Sensitivity dependence on the temperature was tested and the optimum operation temperature was at around 310 $^0$C. The response time for the Pd doped ZnO film was 60 sec and the recovery time was 120 sec. The temperature variation of sensitivity was studied and the maximum sensitivity of 72% was observed at around 300 $^0$C for 1.6 vol% $H_2$ in air.

**KEYWORDS**: SILAR, Pd doped ZnO film, XRD, SEM, EDX, $H_2$.

## I. INTRODUCTION

In gas sensor application zinc oxide (ZnO) is a promising material. ZnO thin films are very good detector of toxic gases, combustible gases and organic vapors. The structural, morphological and electrical characteristics of the films decide the performance and better application of the films. The presence of impurities and defects in the films determined these properties. Pd doped ZnO films have immense applications in optical coatings, solar cells, solid-state display devices and chemical sensors etc [1,2]. Pd is doped due to high transparency, stability, conductivity and it increases the gas-sensing properties of the ZnO thin films [3]. Deposition of Pd doped ZnO thin films has been done by many techniques such as spray pyrolysis [1], pulsed laser deposition [2,4], spin coating [5], sol-gel [6,7,8] etc. The physical techniques give uniform and transparent films. But they are very expensive. On the other hand low-temperature chemical techniques are simple and cheap. One of the less used and less studied chemical techniques is SILAR. In SILAR process we need a substrate and two precursors. One of the precursors contains aqueous solutions of cationic and the other anionic. For the reaction to take place at the substrate surface the substrate should be dipped alternately into the beakers. Depending on the nature and kinetics of the reaction the substrate can be introduced into various reactants for a specific length of time. The number of dipping can be varied differently for different reaction. It limited only by the inherent problems associated with the deposition technique and the substrate-thin film interface. The technique first performed by Call et al (1980) [9] and Ristov et al(1987) [10]. and the name was given by Nicalau et al(1990) [11]. The process involves adsorption of a layer of complex ion on the substrate which is followed by reaction of the adsorbed ion layer. As the technique carried out under mild conditions and at lower temperatures, implantation of dopant at low temperatures may be particularly suitable by this method. The present work is to prepare Pd-doped ZnO thin films on glass substrate by SILAR and study their $H_2$ gas sensing characteristics. V.P.Dravid in his work dealt with the novel Pd doping in ZnO thin film [12]. $Pd^{2+}$ doped ZnO layerd piezoelectric quartz crystal is a detector of ammonia [13]. Pd also has application as a surface catalyst which passivate the defect state on the film and increase the gas sensing performance [14]. In the present work 10% Pd doped ZnO films have been prepared by SILAR. The objective of this work was to deposit Pd doped ZnO films from sodium zincate complex and to study the application potentiality of the films as hydrogen gas sensor. Earlier we have

ISSN: 2277-9655
Impact Factor: 5.164
CODEN: IJESS7

reported the LPG sensing characteristics of Al doped ZnO films following this technique [15]. We have also reported hydrogen and LPG sensing properties $SnO_2$ films [16].

## II. MATERIALS AND METHODS

ZnO and Pd-doped ZnO thin films were prepared on clean glass substrates by SILAR technique. By this technique the substrate dipped in Sodium zincate complex kept at room temperature and hot water bath kept near boiling point alternatively. The Sodium zincate bath prepared by adding Sodium hydroxide pellets (NaOH pellets, Merck, mol. wt 40·00) to Zinc Sulphate ($ZnSO_4$,$7H_2O$) solution. The pH of this solution measured by systronics pH meter (Model 335) was 12.70.

We have reported earlier pure ZnO film deposition from ammonium zincate bath [17,18, 19] and Pd-doped ZnO thin film from sodium zincate bath [20] . A precleaned microscopic glass slide has been taken to dip alternately in zinc complex kept at room temperature and hot water bath maintained at ~94-98.5ºC. One complete set of dipping contains dipping the substrate in each bath for two (2) seconds. 70 dipping were performed for the present experiment. 10% Pd-doped ZnO film was prepared by adding Palladium chloride hexahydrate ($PdCl_2.6H_2O$, Merck) as the source of dopant and was added in requisite amount in the zincate bath. The deposited films were all white and homogeneous. All the prepared films were well adherent on the substrate. The thicknesses of the films were measured by the weight difference-density consideration [10] method. An electronic balance was used for this purpose. The thickness for pure ZnO film was ~ 0.69 μm and it was ~0.89 μm for Pd-doped film. This indicates higher growth rate due to Pd incorporation.

Philips PW 1830 x-ray diffractometer with $CuK_\alpha$ radiation (λ = 1.5418 Å) as X-ray source at 40 kV and 20 mA was used for structural analysis of the deposited films. The experimental peak positions were compared with the standard JCPDS files and the Miller indices were assigned to the peaks. SEM was performed for the morphological characterization of the films. EDX analysis was carried out to check the incorporation of Pd in the doped film. The electrical resistance of the films was measured before and after exposure to $H_2$ using a Keithley System Electrometer (Model: 6514). The sensitivity of the deposited film was observed at different operating temperatures in the range 250-375ºC in presence of $H_2$ in air. Commercially available calibrated mixtures of $H_2$ were used for this purpose. At first the film was equilibrated at each operating temperature for 30 minutes before exposure to $H_2$ gas. The percent sensitivity was measured. For this purpose percent reduction of resistance in presence of the test gas was measured first. If $R_{air}$ and $R_{gas}$ represents the equilibrium sample resistance in ambient air and under test gas respectively, the percent sensitivity $(S\%)$ can be expressed as $S\% = \frac{R_{air} - R_{gas}}{R_{air}} \times 100$ **[**21,22,23**]** The gas sensing characteristics (response and recovery) of the Pd doped ZnO film was carried out for $H_2$. When the ohmic resistance of the sensor material becomes stabilized a known amount of target gas was introduced. The recovery characteristics (when the target gas is withdrawn) as a function of time were also monitored. The sensitivity has been defined as $R_{air}$ /$R_{gas}$ [24, 25, 26] also. It is greater than one (1) for reducing gases since the resistance of a sensor material decreases in presence of reducing gases. In the present work, the sensing characteristic was carried out for a fixed concentration of target gas and we have used the above equation for calculation of sensitivity.

## III. RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffraction (XRD) spectra of undoped and 10% Pd-doped ZnO films. At first the films were annealed at 350ºC for 2 hr. in air before to structural characterization. The diffraction pattern for pure ZnO is shown in figure 1(a), while figure 1(b) shows the pattern for 10% Pd doped ZnO. The diffraction angle 2θ was scanned in the range 20º to 80º. The 2θ variation was employed with a 0.05 degrees step and a time step of 1 second. Intensity in arbitrary units is plotted against 2θ in figure 1. It is seen from figure 1 (a) that peaks appears at 32.21º, 34.94º, 36.59º, 48.50º, 57.60º, 63.88º and 69.02$^0$ . All the peaks are in good agreement with the Joint committee on powder diffraction standard (JCPDS) data belonging to hexagonal $ZnO$ structure [27]. The corresponding reflecting planes are (100), (002), (101), (102), (110), (103) and (112) respectively. For Pd-doped ZnO peaks are at 31.34$^0$, 33.89$^0$,35.68$^0$, 47.61$^0$, 56.73$^0$, 62.98$^0$ and 68.13$^0$. In the XRD patterns there is, no phase corresponding to palladium or other palladium compounds. This suggests that the films do not have any phase segregation or secondary phase formation as well as Pd incorporation into ZnO lattice. The (002) peak appears with maximum intensity in undoped and Pd doped films. This shows that preferred orientation of

ISSN: 2277-9655
Impact Factor: 5.164
CODEN: IJESS7

the crystals along c-axis i.e. perpendicular to the substrate. The other peaks corresponding to (100), (101), (102), (110) ,(103) and (112) are present with low relative intensities.

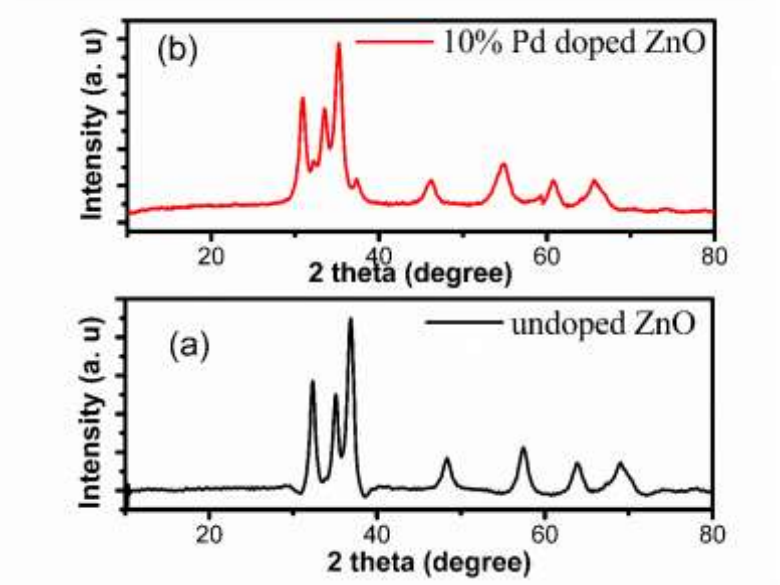


**Figure.1**

Figure 2(a) shows the SEM micrograph of undoped ZnO film. Figure 2(b) shows the SEM image for 10% Pd-doped ZnO films. The incorporation of Pd into the lattice affects the morphology as can be seen from the micrographs. Figure 2(a) shows that the film consists of many round shaped defined uniform grains. However there is agglomeration in certain regions of the film. Figure 2(b) shows particles with off spherical shape. This clears that Pd doping modifies the shape of the grains. Also the Pd doped ZnO film appears to have less porosity compared to un doped ZnO. Thus incorporation of Pd leads to be continuous film with higher density compared to un doped ZnO.

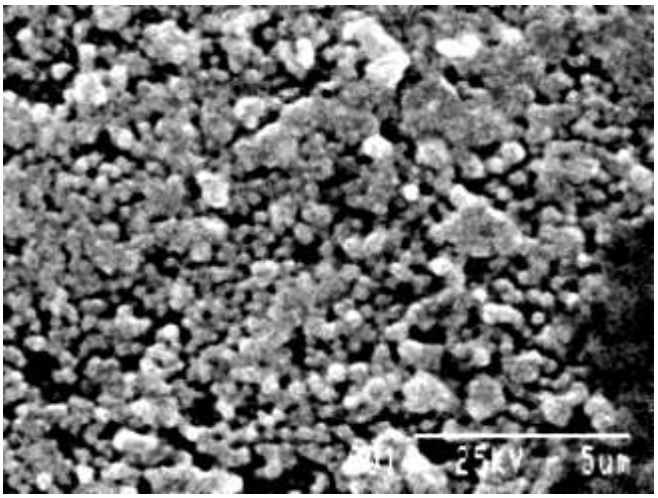


**Figure 2(a): Undoped ZnO**

ISSN: 2277-9655
Impact Factor: 5.164
CODEN: IJESS7

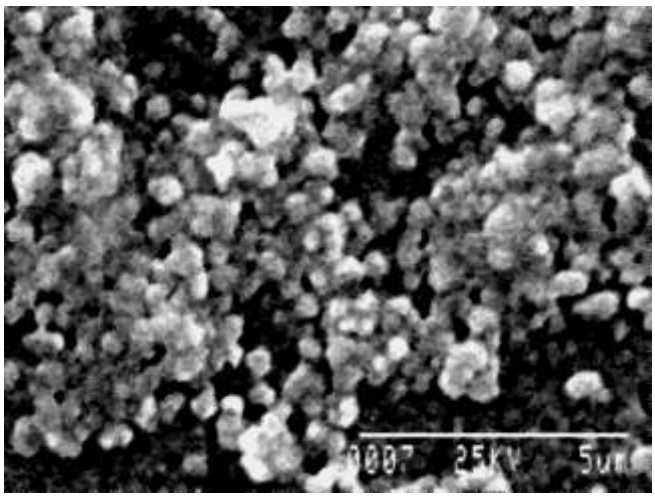

**Figure 2(b): 10%Pd doped ZnO**

The incorporation of Pd in the films was verified by the EDX experiment. Figure 3 shows the energy dispersive X-ray spectrum of palladium doped ZnO film. The spectrum reveals the presence of Zn, O and Pd elements in the deposited films. The silicon signal appears from the substrate.

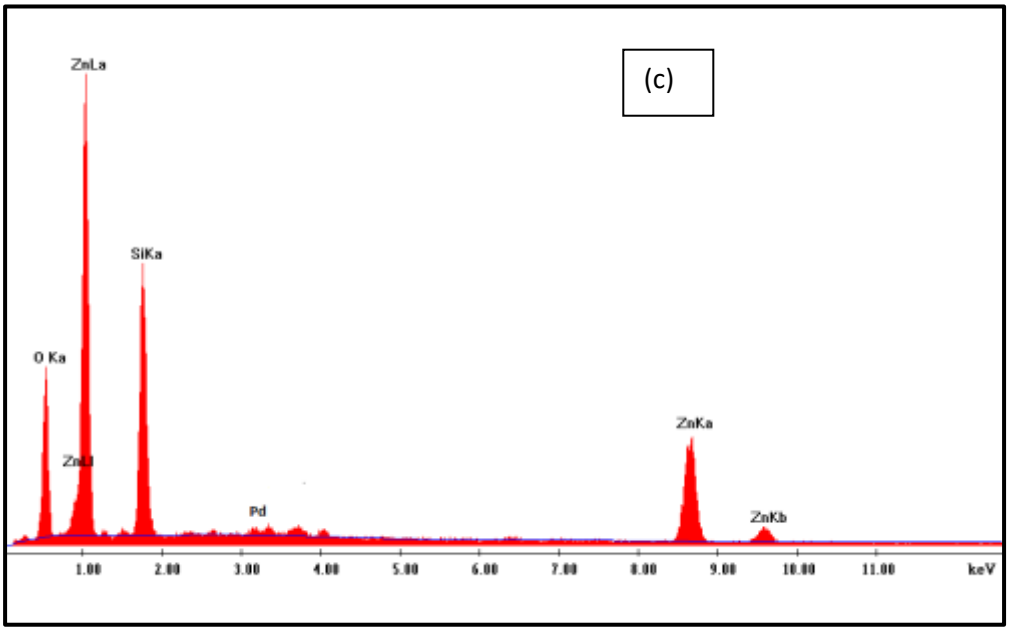


**Figure.3**

Figure 4(a) shows the percent sensitivity (S%) as a function of operating temperature in presence of 1.6 vol% $H_2$ in air. The exposure time to the target gas was 20 minutes. It shows that Pd-doping increases the sensitivity of the films at all temperatures compared to un doped ZnO film. With increasing temperature of the sensor element the sensitivity increases. It reaches a peak value and then decreases again. The peak sensitivity for palladium doped ZnO film was observed at 310ºC and the value of maximum sensitivity was 72%. The plot of resistance

ISSN: 2277-9655
Impact Factor: 5.164
CODEN: IJESS7

ratio $R_{gas}/R_{air}$ against time is shown in the figure 4(b). Faster response (short response time) is given by Pd-doped ZnO compared to un doped ZnO film.

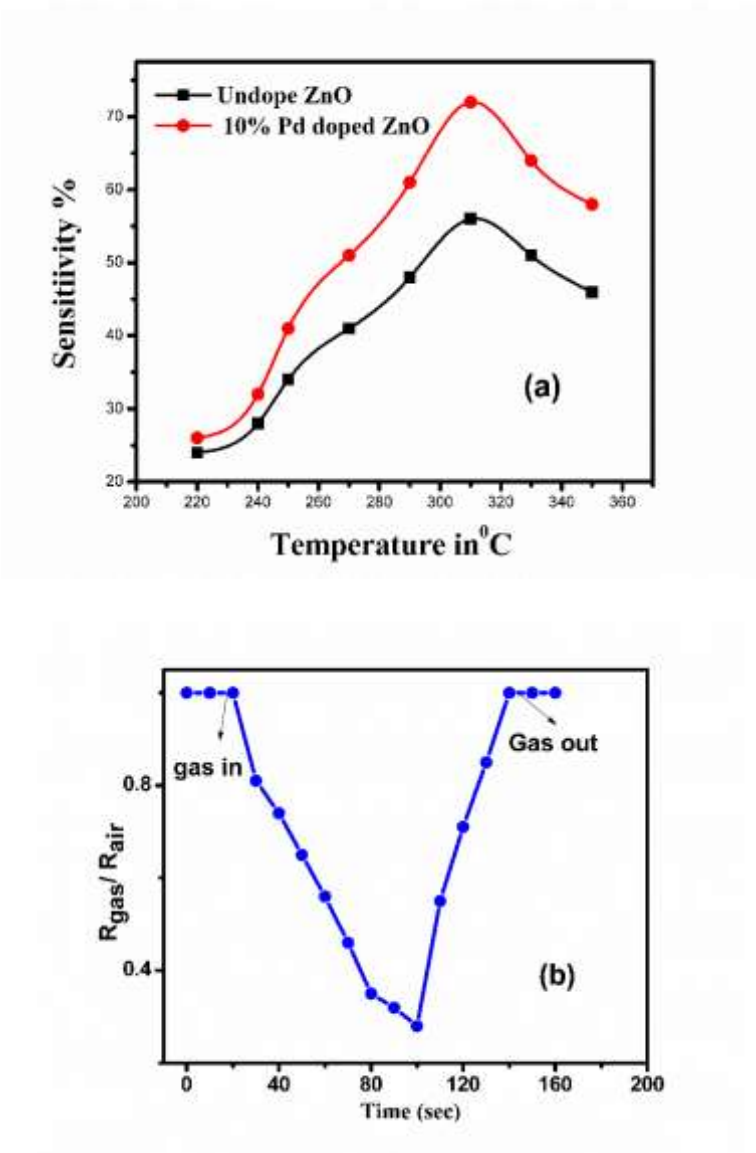


**Figure.4**

The change of sensitivity with operating temperature is probably due to increased speed of chemical reaction between the gas molecules and chemisorbed oxygen species [28]. As the gas molecules have enough thermal energy to react with the chemisorbed species at high temperatures. So we can assume that at temperatures above 325ºC, the number of chemisorbed species available for surface activity is lowered. For which decrease of chemisorbed species can slow down the catalytic oxidation reaction and leads to a decrease in net yield of conduction electrons and also sensitivity.

Pd incorporation enhances the sensitivity which might be due to more porosity of the films. As more porous of the films allows gas molecules to penetrate inside the film and the resistance reduction process continues for a longer time. This delays the attainment of equilibrium resistance value in presence of target gas and increase of response time.

## IV. CONCLUSION

Un doped and Pd-doped ZnO thin film successfully deposited from sodium zincate complex for the first time by SILAR technique. The technique is simple and inexpensive. The method uses milder reaction conditions. Pd doping increases the growth rate of the film. XRD spectra showed that the films have hexagonal structure with preferred c-axis orientation. With temperature the sensitivity of the films increases. It reaches a maximum and then decreases. This phenomenon may be occured due to the change in nature of chemisorbed species with temperature and their number density. A high sensitivity of 72% with a reasonably fast response is observed for Pd doped ZnO film in presence of 1.6 vol% $H_2$ in air. On the other hand due to high resistivity of the Pd-doped ZnO may enhance the gas response of film. [3]

## V. ACKNOWLEDGEMENTS

The author acknowledges department of Physics, The University of Burdwan for providing instrumental facilities.

## VI. REFERENCES

1. Q.G Al-zaidi, A.M Suhail and W.R Al-azawi , “Palladium-doped ZnO thin film hydrogen gas sensor”. *Appl. Phys. Res.* Vol.3, No. 1.pp-89-99 June2011
2. ]. M Kashif, M.E Ali, M Syed, U Ali and U Hashim ,” Sol-gel synthesis of Pd-doped ZnO nanorods for room temperature hydrogen sensing application.”, *Ceramic International* Vol.39,Issue 6, pp- 6461-6466 Aug. 2013
3. N. Al-Hardan, M. J. Abdullah, A. Abdul Aziz, “The gas response enhancement from ZnO film for $H_2$ gas detection”, Appl. Surf. Sci. Vol.255,Issue 17, pp.7794-7797 June 2009
4. S. Y. Lee, Y. Li, J.-S. Lee et al., “Effects of chemical composition on the optical properties of Zn1−*x*Cd*x*O thin films,” *Applied Physics Letters*, vol. 85, no. 2, pp. 218–220, 2004.
5. A Gupta, S Gangopadhyay, K Gangopadhyay and S Bhattacharya, “Palladium –functionalized nanostructured platforms for enhanced hydrogen sensing.” *Nano mater. Nano tech*. .Vol.6, pp.1-11. April 2016
6. R.H Thaher , G.M Ali and A.A Abdullaleef , *J of Eng and Development* Vol. 20, pp. 1-11(2016)
7. M Kumar, V.S Bhati, S Ranwa, J Singh and M Kumar, “Pd/ZnO nanorods based sensor for highly selective detection of extremely low concentration hydrogen.”*Scientific Reports* , Vol. 7.No.236, pp-1-9. Feb 2017.
8. G.M Ali, C.V Thompson, A.K Jasim, I.M Abdulbaqi and J.C Moore. “Effect of embedded Pd microstructures on the flat-band-voltage operation of room temperature ZnO based liquid Petroleum gas sensors.” *Sensors* Vol.13, Issue 12. Pp-16801-16815. Dec2013
9. R.L Call , N.K Jaber, K Seshan and J.R Whyte, “Structural and electronic properties of three aqueous deposited films : CdS, CdO, ZnO for semiconductor and photovoltaic applications.” *Solar Energy Mater*. Vol.2, Issue 3 pp.-373-380. June 1980.
10. M Ristov , G.J Sinadinovski , I Grozdanov and M Mitreski, “Chemical deposition of ZnO films.” *Thin Solid Films* . Vol.149 Issue 1, pp- 65-71. May1987
11. Y.F. Nicolau , M Dupuy and M, J. Brunel , “ZnS, CdS, and $_{Zn1-x}Cd_xS$ thin films deposited by the successive ionic layer adsorption and reaction process.”. *Eletrochem Soc*. Vol.137, pp.-2915-2925 March1990
12. V. P. Dravid, S.-W. Fan, S. Sathananthan; Nanoscape 6 (2009).
13. X. Wang, J. Zhang, Z. Zhu, J. Zhu, “Effects of $Pd^{2+}$ doping on ZnO nanotetrapods ammonia sensor” Colloids and Surfaces A: Physicochem. Eng. Aspects Vol. 276 Issue 1-3 pp. 59–64.2006
14. K. Nomura, H. Ohta, K. Ueda, T. Kamiya, M. Hirano, H. Hosono, “Thin-film transistor fabricated in single-crystalline transparent oxide semiconductor.” , ScienceVol. 300 No. 5623pp. 1269-1272 .2003
15. **Shampa Mondal, Shatabda Bhattacharya, and P.Mitra, “**Structural, Morphological, and LPG Sensing Properties of Al-Doped ZnO Thin Film Prepared by SILAR.” Advances in Materials Science and Engineering Vol. 2013. Pp 1-6 dx.doi.org/10.115/2013/382380
16. P. MITRA_ and S. MONDAL , “Hydrogen and LPG sensing properties of SnO2 films obtained by direct oxidation of SILAR deposited SnS.”, BULLETIN OF THE POLISH ACADEMY OF SCIENCESn TECHNICAL SCIENCES Vol. 56, No. 3, pp 295-300. 2008
17. P. Mitra, “Preparation of ZnO film on p-Si substrate and I-V characteristics of p-Si/n-ZnO,” *Material Science Research India*, vol. 8, pp. 197–202, 2011

18. P. Mitra and J. Khan, "Chemical deposition of ZnO films from ammonium zincate bath,"*Materials Chemistry and Physics*, vol. 98, no. 2-3, pp. 279–284, 2006.
19. S. Mondal and P. Mitra, "Preparation of cadmium doped ZnO thin films by SILAR and their characterization," *Bulletin of Materials Science*, vol. 35, pp. 751–757, 2012.
20. S. Mondal, " PALLADIUM DOPED ZNO THIN FILMS PREPARED BY SILAR AND THEIR STRUCTURAL, OPTICAL CHARACTERIZATION". *INTERNATIONAL JOURNAL OF ENGINEERING SCIENCES & RESEARCH TECHNOLOGY, 7*(2), 696-701.Feb 2018
21. D. Lee, H. Jung, J. Kim, M. Lee, S. Ban, J. Huh, and D. Lee,"Explosive gas recognition system using thick film sensor array and neural network", Sensors and Actuators B 71, 90–98(2000).
22. H. Nanto, T. Minami,and S. Takata, "Ammonia. gas sensor using sputtered zinc oxide thin film", J. Appl. Phys. 60, 482–484July (1986)
23. L. Jianping, W. Yue, G. Xiaoguang, M. Qing, W. Li, and H. Jinghong, 'H2S sensing properties of the SnO2-based thin films", Sensors and Actuators 65, 111–113 (2000).
24. J.H. Yu, and G.M. Choi, "Selective CO gas detection of CuO and ZnO-doped SnO2gas sensor", Sensors and Actuators 75, 56–61 (2001).
25. K.H. Song and S.J. Park, "Gas sensing characteristics of tin dioxide with small crystallites", J. Materials Science: Materials in Electronics 4, 249–253 (1993).
26. N.S. Baik, G. Sakai, K. Shimanoe, N. Miura, and N. Yamazoe, "Hydrothermal treatment of tin oxide sol solution for preparation of thin-film sensor with enhanced thermal stability and gas sensitivity", Sensors and Actuators B 65, 97–100 (2000).
27. Joint Committee on Powder Diffraction standards, "Inorganic," B. Post, S.Weissmann, and H. F.McMurdie, Eds., Card No. 361451, InternationalCentre forDiffractionData, Swarthmore, Pa, USA, 1990.
28. J. C. Simpson and J. F. Cordaro, "Characterization of deep levels in zinc oxide," *Journal of Applied Physics*, vol. 63, no. 5, pp. 1781–1783, 1988

.

## CITE AN ARTICLE

Mondal, S. (n.d.). SURFACE MORPHOLOGICAL, STRUCTURAL AND HYDROGEN SENSING CHARACTERIZATION OF PD DOPED ZnO THIN FILMS DEPOSITED BY SILAR. *INTERNATIONAL JOURNAL OF ENGINEERING SCIENCES & RESEARCH TECHNOLOGY,7*(3), 456-462.